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THE THEORY OF DIFFUSION IN STRAINED SYSTEMS

By LOUIS A. GIRIFALCO and HUBERT H. GRIMES

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SUMMARY

Because the current theory of solid-state diffusion is limited to unstrained crystals and cannot be applied readily to strained systems, Fick's first and second laws were generalized to include the effects of strain on the diffusion rates. The nonhomogeneity introduced into the atomic jump frequency by strain was found to contribute strain-dependent terms to the diffusion equations in addition to the terms containing the concentration gradient.

From a consideration of the effect of strain on the free energy of activation, it can be shown that for simple strains, such as those resulting from compression, tension, shear, and hydrostatic pressure, the diffusion coefficient is an exponential function of the lattice parameter. An examination of the available experimental data for the variation of diffusion coefficients with pressure confirms this theoretical prediction.

The theory presented herein states that the magnitude of the variation of the diffusion coefficient with pressure depends on the interatomic forces as the diffusing atom moves from its equilibrium position to the activated position. On the basis of this theory, a parameter depending upon the interatomic forces can be computed from the experimental data. In all cases investigated, the magnitudes of this parameter were in agreement with the known characteristics of the interatomic potential-energy functions of the systems.

The effect of plastic flow on the diffusion rate was also studied by considering the rate at which vacancies are produced by dislocation motion and the rate at which vacancies condense at inhomogeneities in the crystal. The resulting equations predict that for a vacancy mechanism the diffusion coefficient varies linearly with the strain rate. This conclusion is in agreement with experiment.

INTRODUCTION

The theory of diffusion in solids has been the subject of a great deal of investigation in recent years, and satisfactory theoretical models have been constructed that adequately describe the basic diffusion processes in many simple solids. Present theories, however, are limited to unstrained crystals and are not strictly applicable to strained systems. Since the diffusion rate is determined by the energy of interaction between the diffusing atom and the crystal lattice, and since this energy depends on the interatomic distances, it is to be expected that the diffusion coefficients will be altered by a strain superimposed on the crystal. Some experimental evidence is available that indicates that elastic strain can increase the self-diffusion coefficient by as much as a factor of 2 (ref. 1) and that plastic strain can increase the self-diffusion coefficient by an order of magnitude (refs. 2 and 3). Also, it is well known that hydrostatic pressure decreases the diffusion coefficient; in fact, a pressure of 7500 atmospheres is sufficient to lower the self-diffusion coefficient of sodium by an order of magnitude at 90° C (ref. 4).

If the crystal is strained in a nonhomogeneous manner, another factor becomes operative in addition to those that control the change in the diffusion coefficient. According to the theory of irreversible processes (ref. 5), every thermodynamic flux is proportional to every thermodynamic force, so that the diffusion flux is not only proportional to the concentration gradients, but is also proportional to the strain gradients in the crystal. Thus, not only is the magnitude of the diffusion coefficient changed by a generalized strain, but the basic character of the diffusion equations is also changed.

Because of the important role played by diffu-

¹Supersedes NACA Technical Note 4408 by Louis A. Girifalco and Hubert H. Grimes, 1958.

sion processes in many solid-state phenomena such as oxidation, the annealing of radiation damage, creep, and rupture, and in view of the wide variety of applications in which materials are under strain, a thorough understanding of the effects of strain on diffusion is highly desirable.

In this report the theory of diffusion in strained systems is developed from the point of view of molecular kinetics, the fundamental physical factors involved are discussed, and the resulting theory is compared with existing experimental data.

BASIC EQUATIONS OF DIFFUSION THEORY

Generalizations of Fick's first and second laws are obtained for the diffusion of a single species in a crystalline lattice by a modification of the method of conditional transition probabilities (ref. 6). The diffusion equations are expressed in terms of atomic jump frequencies without the usual condition that the jump frequency is independent of position. In this form, the equations can easily be applied to a strained lattice.

Consider a volume element $d\vec{r}$ in the crystal centered about the point defined by the position vector \vec{r} . The number of particles of the diffusing species contained in $d\vec{r}$ is given by $N(\vec{r}, t)d\vec{r}$, where $N(\vec{r}, t)$ is the concentration of diffusing species at the position \vec{r} and time t . In general, the number of particles in the volume element $d\vec{r}$ is not constant, because particles are continually jumping out of $d\vec{r}$ while other particles are jumping into $d\vec{r}$ from adjacent portions of the crystal. The rate at which $N(\vec{r}, t)$ changes as a result of these two processes can be calculated as follows: If $\Lambda(\vec{r}, \vec{r}', t)d\vec{r}' dt$ is the conditional probability that an atom in the volume element $d\vec{r}$ jumps to the volume element $d\vec{r}'$ during time dt , then the number of particles that jump from $d\vec{r}$ to $d\vec{r}'$ in time dt is given by

$$N(\vec{r}, t)\Lambda(\vec{r}, \vec{r}', t)d\vec{r} d\vec{r}' dt \quad (1)$$

and the total number of particles that jump out of $d\vec{r}$ during time dt is obtained by integrating overall $d\vec{r}'$; that is,

$$N_-(\vec{r}, t)d\vec{r} dt = N(\vec{r}, t)d\vec{r} dt \int_{\vec{r}'} \Lambda(\vec{r}, \vec{r}', t)d\vec{r}' \quad (2)$$

where $N_-(\vec{r}, t)$ is the rate at which particles leave the volume element $d\vec{r}$.

Similarly, the number of particles that jump from $d\vec{r}'$ to $d\vec{r}$ during time dt is given by

$$N(\vec{r}', t)\Lambda(\vec{r}', \vec{r}, t)d\vec{r}' d\vec{r} dt \quad (3)$$

and the total number of particles that jump into $d\vec{r}$ from other parts of the crystal is given by

$$N_+(\vec{r}, t)d\vec{r} dt = d\vec{r} dt \int_{\vec{r}'} N(\vec{r}', t)\Lambda(\vec{r}', \vec{r}, t)d\vec{r}' \quad (4)$$

where $N_+(\vec{r}, t)$ is the rate at which particles enter the element $d\vec{r}$. The net rate of increase of $N(\vec{r}, t)$ is obtained by subtracting equation (2) from equation (4):

$$\frac{\partial N}{\partial t} = \int_{\vec{r}'} N(\vec{r}', t)\Lambda(\vec{r}', \vec{r}, t)d\vec{r}' - N(\vec{r}, t) \int_{\vec{r}'} \Lambda(\vec{r}, \vec{r}', t)d\vec{r}' \quad (5)$$

At this point it is convenient to express equation (5) in terms of the jump distance $(\vec{r}' - \vec{r})$ by performing a transformation of variables so that

$$\vec{X} = \vec{r}' - \vec{r} \quad (6)$$

In terms of the jump vector \vec{X} , equation (5) becomes

$$\frac{\partial N}{\partial t} = \int_{\vec{X}} N(\vec{r} + \vec{X}, t)\Lambda(\vec{r} + \vec{X}, \vec{r}, t)d\vec{X} - N(\vec{r}, t) \int_{\vec{X}} \Lambda(\vec{r}, \vec{r} + \vec{X}, t)d\vec{X} \quad (7)$$

The function $\Lambda(\vec{r} + \vec{X}, \vec{r}, t)$ is the probability frequency that a particle at $\vec{r} + \vec{X}$ will jump to \vec{r} ; and if the vector \vec{X} would always terminate at a point that is capable of accommodating the diffusing particle, Λ would equal the atomic jump frequency. There are cases, however, such as in diffusion by the vacancy mechanism, in which the terminus of \vec{X} cannot always accommodate the

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migrating particle. The jump frequency must then be multiplied by the probability that a vacant site exists at the end of the atomic jump. Therefore, if $\Gamma(\vec{r}, \vec{X})$ is the atomic jump frequency with jump vector \vec{X} and $n(\vec{r}, t)$ is the probability that a site at \vec{r} is vacant (i.e., it can accept the jumping particle), then,

$$\left. \begin{aligned} \Lambda(\vec{r} + \vec{X}, \vec{r}, t) &= \Gamma(\vec{r} + \vec{X}, -\vec{X})n(\vec{r}, t) \\ \Lambda(\vec{r}, \vec{r} + \vec{X}, t) &= \Gamma(\vec{r}, \vec{X})n(\vec{r} + \vec{X}, t) \end{aligned} \right\} \quad (8)$$

Substituting equation (8) into equation (7) and arbitrarily replacing \vec{X} with the equally valid negative argument $-\vec{X}$ in the first integral of equation (7) give

$$\frac{\partial N}{\partial t} = n(\vec{r}, t) \int_{\vec{X}} N(\vec{r} - \vec{X}, t) \Gamma(\vec{r} - \vec{X}, \vec{X}) d\vec{X} \\ - N(\vec{r}, t) \int_{\vec{X}} \Gamma(\vec{r}, \vec{X}) n(\vec{r} + \vec{X}, t) d\vec{X} \quad (9)$$

In crystalline solids, Γ is zero for all jump vectors except for a small number of \vec{X} 's, which may be denoted by $\vec{\lambda}_i$; Γ may then be expressed as a delta function:

$$\Gamma(\vec{r}, \vec{X}) = \sum_{i=1}^a \Gamma_i(\vec{r}) \delta(\vec{X} - \vec{\lambda}_i) \quad (10)$$

where a is the total number of possible jumps a particle can make out of its position at \vec{r} . The set of possible jump vectors $\vec{\lambda}_i$ and the value of a are determined by the crystal structure of the lattice. Substituting equation (10) into equation (9) and making use of the properties of the delta function yield

$$\frac{\partial N}{\partial t} = n(\vec{r}, t) \int_{\vec{X}} N(\vec{r} - \vec{X}, t) \sum_{i=1}^a \Gamma_i(\vec{r} - \vec{X}) \delta(\vec{X} - \vec{\lambda}_i) d\vec{X} \\ - N(\vec{r}, t) \int_{\vec{X}} \sum_{i=1}^a \Gamma_i(\vec{r}) \delta(\vec{X} - \vec{\lambda}_i) n(\vec{r} + \vec{X}, t) d\vec{X} \\ = n(\vec{r}, t) \sum_{i=1}^a \Gamma_i(\vec{r} - \vec{\lambda}_i) \Gamma_i(\vec{r} - \vec{\lambda}_i) \\ - N(\vec{r}, t) \sum_{i=1}^a \Gamma_i(\vec{r}) n(\vec{r} + \vec{\lambda}_i, t) \quad (11)$$

It will now be assumed that the functions $N\Gamma$ and n can be expressed as a Taylor expansion in powers of $\vec{\lambda}_i$ about the point \vec{r} , retaining only the first three terms of the expansion. Therefore,

$$N(\vec{r} - \vec{\lambda}_i, t) \Gamma_i(\vec{r} - \vec{\lambda}_i) = N(\vec{r}, t) \Gamma_i(\vec{r}) \\ - \vec{\lambda}_i \cdot \nabla N \Gamma_i + \frac{1}{2} (\vec{\lambda}_i \cdot \nabla)^2 N \Gamma_i \quad (12)$$

and

$$n(\vec{r} + \vec{\lambda}_i, t) = n(\vec{r}, t) + \vec{\lambda}_i \cdot \nabla n + \frac{1}{2} (\vec{\lambda}_i \cdot \nabla)^2 n \quad (13)$$

The derivatives are evaluated at the point \vec{r} . Equation (11) now can be written as

$$\frac{\partial N}{\partial t} = n(\vec{r}, t) N(\vec{r}, t) \sum_{i=1}^a \Gamma_i(\vec{r}) - n(\vec{r}, t) \sum_{i=1}^a \vec{\lambda}_i \cdot \nabla N \Gamma_i \\ + \frac{1}{2} n(\vec{r}, t) \sum_{i=1}^a (\vec{\lambda}_i \cdot \nabla)^2 N \Gamma_i \\ - n(\vec{r}, t) N(\vec{r}, t) \sum_{i=1}^a \Gamma_i(\vec{r}) - N(\vec{r}, t) \sum_{i=1}^a \Gamma_i(\vec{r}) \vec{\lambda}_i \cdot \nabla n \\ - \frac{1}{2} N(\vec{r}, t) \sum_{i=1}^a \Gamma_i(\vec{r}) (\vec{\lambda}_i \cdot \nabla)^2 n \quad (14)$$

or

$$\frac{\partial N}{\partial t} = \sum_{i=1}^a \left\{ -(\vec{\lambda}_i \cdot \nabla) (n N \Gamma_i) \right. \\ \left. + \frac{1}{2} [n (\vec{\lambda}_i \cdot \nabla)^2 N \Gamma_i - N \Gamma_i (\vec{\lambda}_i \cdot \nabla)^2 n] \right\} \quad (15)$$

Equation (15) is a generalization of Fick's second law and is valid for any system regardless of the nature of $\vec{\lambda}_i$ or of the coordinate system chosen. Also, if the strain is homogeneous, $\nabla \Gamma_i = 0$. With these restrictions, equation (15) reduces to

$$\frac{\partial N}{\partial t} = \frac{1}{2} n(\vec{r}, t) \sum_{i=1}^a \Gamma_i(\vec{r}) (\vec{\lambda}_i \cdot \nabla)^2 N \\ - \frac{1}{2} N(\vec{r}, t) \sum_{i=1}^a \Gamma_i(\vec{r}) (\vec{\lambda}_i \cdot \nabla)^2 n \quad (16)$$

The position vector \vec{r} in equation (16) is referred to an arbitrary coordinate system. It is always possible to find a transformation of coordinates so that the position vector is referred to the principal axes of diffusion in which mixed derivatives, such as $\partial^2 N / \partial x \partial y$, vanish.

In this case,

$$\begin{aligned} \frac{\partial N}{\partial t} = & \frac{n(r,t)}{2} \sum_{i=1}^a \Gamma_i \left(\lambda_{ix}^2 \frac{\partial^2 N}{\partial x^2} + \lambda_{iy}^2 \frac{\partial^2 N}{\partial y^2} + \lambda_{iz}^2 \frac{\partial^2 N}{\partial z^2} \right) \\ & - \frac{N(r,t)}{2} \sum_{i=1}^a \Gamma_i \left(\lambda_{ix}^2 \frac{\partial^2 n}{\partial x^2} + \lambda_{iy}^2 \frac{\partial^2 n}{\partial y^2} + \lambda_{iz}^2 \frac{\partial^2 n}{\partial z^2} \right) \end{aligned} \quad (17)$$

where λ_{ix} , λ_{iy} , and λ_{iz} are the components of $\vec{\lambda}_i$. The coordinates are now referred to the principal axes of diffusion.

Since Fick's first and second laws are connected by the equation of continuity,

$$\frac{\partial N}{\partial t} = -\nabla \cdot \vec{J}_N \quad (18)$$

where \vec{J}_N is the flux of species N , Fick's first law corresponding to the second law given by equation (17) is

$$\left. \begin{aligned} J_x = & -\frac{n(r,t)}{2} \sum_{i=1}^a \Gamma_i \lambda_{ix}^2 \frac{\partial N}{\partial x} + \frac{N(r,t)}{2} \sum_{i=1}^a \Gamma_i \lambda_{ix}^2 \frac{\partial n}{\partial x} \\ J_y = & -\frac{n(r,t)}{2} \sum_{i=1}^a \Gamma_i \lambda_{iy}^2 \frac{\partial N}{\partial y} + \frac{N(r,t)}{2} \sum_{i=1}^a \Gamma_i \lambda_{iy}^2 \frac{\partial n}{\partial y} \\ J_z = & -\frac{n(r,t)}{2} \sum_{i=1}^a \Gamma_i \lambda_{iz}^2 \frac{\partial N}{\partial z} + \frac{N(r,t)}{2} \sum_{i=1}^a \Gamma_i \lambda_{iz}^2 \frac{\partial n}{\partial z} \end{aligned} \right\} \quad (19)$$

where J_x , J_y , and J_z are the components of \vec{J}_N .

The physical significance of the theoretical development up to this point can be seen most clearly by a consideration of equation (14). In the usual expression for Fick's second law in unstrained systems, all terms except those involving the second derivative of N are zero. The other terms appear in equation (14), however, because it was not assumed in the present development that Γ_i and n are independent of position. The second term does not sum to zero since, in general, it is not composed of terms antisymmetric in $\vec{\lambda}_i$. Furthermore, since Γ_i and n are functions of position, they must be retained in the differential operators, and terms dependent on the first and second derivatives of Γ_i and n appear in equation (14).

In the case of a uniform homogeneous strain, equation (14) reduces to equation (17). If the gradient of n is zero, equation (17) becomes equivalent to Fick's second law. In this simple case,

it is necessary only to calculate the effect of the homogeneous strain on Γ_i and n in order to specify the effect of strain on diffusion. The effect of strain on the jump frequency can be analyzed in terms of rate theory. This analysis is presented in the following section. The effect of strain on n is dependent upon the diffusion mechanism. For interstitial diffusion, $n = 1$ provided that the concentration of interstitials is low and that strains do not affect this value. For diffusion by a vacancy mechanism, however, n is the vacancy concentration and will vary with strain. An analysis of this variation is presented in the section **DEPENDENCE OF VACANCY CONCENTRATION ON STRAIN**.

DEPENDENCE OF JUMP FREQUENCY ON STRAIN

According to the statistical theory of rate processes, the jump frequency is determined by the ratio of two configurational partition functions, one referring to the activated state and the other referring to the normal state. In analyzing the effect of strain on the jump frequency, the formulation of the rate process theory in solids given in reference 7 is used in which the jump frequency is given by

$$\Gamma = \left(\frac{kT}{2\pi} \right)^{1/2} \frac{\int_{\sigma} \exp(-\varphi/kT) d\sigma}{\int_v \exp(-\varphi/kT) dv} \quad (20)$$

where k is Boltzmann's constant, T is the temperature, and φ is the potential energy of the system as a function of all the coordinates of all the atoms in the crystal. The integral in the numerator of equation (20) is evaluated over a hypersurface σ in the configuration space so that the surface passes through the point corresponding to the diffusing atom at its activated position with all other atoms at their equilibrium position. The hypersurface is also required to be perpendicular to contours of constant potential energy in the configuration space. The hypersurface defined in this manner divides the configuration space into two symmetric parts. The integral in the denominator is evaluated over the configuration volume v of one of these symmetric parts.

Equation (20) was derived for the case of an unstrained crystal. However, it is applicable to strained crystals if the potential energy φ is taken to be a function of the six strain components

$\epsilon_{\alpha\beta}$ as well as the atomic coordinates q_i . A similar procedure has been used in reference 8 in an analysis of the statistical mechanics of crystal lattices. Thus, the potential energy in equation (20) is given by

$$\varphi = \varphi(q_i, \epsilon_{\alpha\beta}) \quad (21)$$

where q_i represents the set of all atomic coordinates and $\epsilon_{\alpha\beta}$ represents the set of six independent strain components.

The potential φ can be expanded in a Taylor series about the normal lattice configuration in the unstrained state to give

$$\begin{aligned} \varphi = & \varphi(q_j^0, 0) + \sum_j \left(\frac{\partial \varphi}{\partial q_j} \right)_{0,0} \delta q_j + \sum_{\alpha,\beta} \left(\frac{\partial \varphi}{\partial \epsilon_{\alpha\beta}} \right)_{0,0} \epsilon_{\alpha\beta} \\ & + \frac{1}{2} \sum_{j,k} \left(\frac{\partial^2 \varphi}{\partial q_j \partial q_k} \right)_{0,0} \delta q_j \delta q_k + \frac{1}{2} \sum_{\alpha,\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\gamma\delta}} \right)_{0,0} \epsilon_{\alpha\beta} \epsilon_{\gamma\delta} \\ & + \sum_{j,\alpha,\beta} \delta q_j \epsilon_{\alpha\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial q_j} \right)_{0,0} + \dots \quad (22) \end{aligned}$$

where q_j^0 represents the set of atomic coordinates when all the atoms are in their mean positions for the normal state of the crystal, and the double zero subscript indicates that the derivatives are evaluated at the point $(q_j^0, 0)$.

If the potential energy is expanded about the point $(q_j^{\ddagger}, 0)$, where q_j^{\ddagger} represents the mean atomic coordinates when the system is in the activated state, then

$$\begin{aligned} \varphi = & \varphi(q_j^{\ddagger}, 0) + \sum_j \left(\frac{\partial \varphi}{\partial q_j} \right)_{\ddagger,0} \delta q_j + \sum_{\alpha,\beta} \left(\frac{\partial \varphi}{\partial \epsilon_{\alpha\beta}} \right)_{\ddagger,0} \epsilon_{\alpha\beta} \\ & + \frac{1}{2} \sum_{j,k} \left(\frac{\partial^2 \varphi}{\partial q_j \partial q_k} \right)_{\ddagger,0} \delta q_j \delta q_k + \frac{1}{2} \sum_{\alpha,\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\gamma\delta}} \right)_{\ddagger,0} \epsilon_{\alpha\beta} \epsilon_{\gamma\delta} \\ & + \sum_{j,\alpha,\beta} \delta q_j \epsilon_{\alpha\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial q_j} \right)_{\ddagger,0} + \dots \quad (23) \end{aligned}$$

The subscript $\ddagger, 0$ indicates that the derivatives are evaluated at the point $(q_j^{\ddagger}, 0)$.

Since the point $(q_j^0, 0)$ corresponds to an unstrained crystal with all atoms in a mean position so that the crystal is at the bottom of a potential well, the first derivatives in equation (22) vanish:

$$\left(\frac{\partial \varphi}{\partial q_j} \right)_{0,0} = \left(\frac{\partial \varphi}{\partial \epsilon_{\alpha\beta}} \right)_{0,0} = 0 \quad (24)$$

The point $(q_j^{\ddagger}, 0)$ corresponds to a saddle point with respect to the atomic coordinates q_j , so that

the derivative of φ with respect to q_j also vanishes at this point. However, $(q_j^{\ddagger}, 0)$ is not a saddle point or a minimum point with respect to the strains, and therefore the derivative at this point with respect to the strains does not vanish:

$$\left(\frac{\partial \varphi}{\partial q_j} \right)_{\ddagger,0} = 0 \quad (25)$$

$$\left(\frac{\partial \varphi}{\partial \epsilon_{\alpha\beta}} \right)_{\ddagger,0} \neq 0 \quad (26)$$

Equations (22) and (23) therefore become

$$\begin{aligned} \varphi = & \varphi(q_j^0, 0) + \frac{1}{2} \sum_{j,k} \left(\frac{\partial^2 \varphi}{\partial q_j \partial q_k} \right)_{0,0} \delta q_j \delta q_k \\ & + \frac{1}{2} \sum_{\alpha,\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\gamma\delta}} \right)_{0,0} \epsilon_{\alpha\beta} \epsilon_{\gamma\delta} \\ & + \sum_{j,\alpha,\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial q_j} \right)_{0,0} \delta q_j \epsilon_{\alpha\beta} + \dots \quad (27) \end{aligned}$$

and

$$\begin{aligned} \varphi = & \varphi(q_j^{\ddagger}, 0) + \sum_{\alpha,\beta} \left(\frac{\partial \varphi}{\partial \epsilon_{\alpha\beta}} \right)_{\ddagger,0} \epsilon_{\alpha\beta} \\ & + \frac{1}{2} \sum_{j,k} \left(\frac{\partial^2 \varphi}{\partial q_j \partial q_k} \right)_{\ddagger,0} \delta q_j \delta q_k \\ & + \frac{1}{2} \sum_{\alpha,\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\gamma\delta}} \right)_{\ddagger,0} \epsilon_{\alpha\beta} \epsilon_{\gamma\delta} \\ & + \sum_{j,\alpha,\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial q_j} \right)_{\ddagger,0} \delta q_j \epsilon_{\alpha\beta} + \dots \quad (28) \end{aligned}$$

Substituting equations (27) and (28) into the denominator and numerator of equation (20), respectively, gives

$$\Gamma_s = \left(\frac{kT}{2\pi} \right)^{1/2} g(\epsilon) \frac{\int_a^b f_{\ddagger}(q) \exp \left[-\frac{1}{kT} \sum_{j,\alpha,\beta} \delta q_j \epsilon_{\alpha\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial q_j} \right)_{\ddagger,0} \right] d\sigma}{\int_a^b f_0(q) \exp \left[-\frac{1}{kT} \sum_{j,\alpha,\beta} \delta q_j \epsilon_{\alpha\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial q_j} \right)_{0,0} \right] dr} \quad (29)$$

where Γ_s is the jump frequency in the strained system and where the functions $g(\epsilon)$, $f_{\ddagger}(q)$, and $f_0(q)$ are defined by

$$\begin{aligned} g(\epsilon) = & \exp \left\{ -\frac{1}{kT} \sum_{\alpha,\beta} \left(\frac{\partial \varphi}{\partial \epsilon_{\alpha\beta}} \right)_{\ddagger,0} \epsilon_{\alpha\beta} \right. \\ & \left. - \frac{1}{2kT} \sum_{\alpha,\beta} \epsilon_{\alpha\beta} \epsilon_{\gamma\delta} \left[\left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\gamma\delta}} \right)_{\ddagger,0} \right. \right. \\ & \left. \left. - \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\gamma\delta}} \right)_{0,0} \right] \right\} \quad (30) \end{aligned}$$

and

$$f_{\ddagger}(q) = \exp \left[-\frac{1}{kT} \varphi(q_{\ddagger}, 0) - \frac{1}{2kT} \sum_{j,k} \left(\frac{\partial^2 \varphi}{\partial q_j \partial q_k} \right)_{\ddagger,0} \delta q_j \delta q_k \right] \quad (31)$$

and

$$f_0(q) = \exp \left[-\frac{1}{kT} \varphi(q, 0) - \frac{1}{2kT} \sum_{j,k} \left(\frac{\partial^2 \varphi}{\partial q_j \partial q_k} \right)_{0,0} \delta q_j \delta q_k \right] \quad (32)$$

The functions $f_{\ddagger}(q)$ and $f_0(q)$ are the Boltzmann factors of the potential energy expanded about the saddle point of the activated state and about the minimum of the normal crystal. Therefore, in the unstrained case, equation (20) may be written as

$$\Gamma_u = \left(\frac{kT}{2\pi} \right)^{1/2} \frac{\int_{\sigma} f_{\ddagger}(q) d\sigma}{\int_{\sigma} f_0(q) d\sigma} \quad (33)$$

Therefore, multiplying and dividing equation (29) by Γ_u , the jump frequency in the unstrained crystal, give

$$\Gamma_s = \Gamma_u g(\epsilon) \frac{\left\langle \exp \left[-\frac{1}{kT} \sum_{j,\alpha,\beta} \delta q_j \epsilon_{\alpha\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial q_j} \right)_{\ddagger,0} \right] \right\rangle_{\sigma}}{\left\langle \exp \left[-\frac{1}{kT} \sum_{j,\alpha,\beta} \delta q_j \epsilon_{\alpha\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial q_j} \right)_{0,0} \right] \right\rangle_{\sigma}} \quad (34)$$

where the statistical mechanical averages are given by

$$\left\langle \exp \left[-\frac{1}{kT} \sum_{j,\alpha,\beta} \delta q_j \epsilon_{\alpha\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial q_j} \right)_{\ddagger,0} \right] \right\rangle_{\sigma} = \frac{\int_{\sigma} f_{\ddagger}(q) \exp \left[-\frac{1}{kT} \sum_{j,\alpha,\beta} \delta q_j \epsilon_{\alpha\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial q_j} \right)_{\ddagger,0} \right] d\sigma}{\int_{\sigma} f_{\ddagger}(q) d\sigma} \quad (35)$$

and

$$\left\langle \exp \left[-\frac{1}{kT} \sum_{j,\alpha,\beta} \delta q_j \epsilon_{\alpha\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial q_j} \right)_{0,0} \right] \right\rangle_{\sigma} = \frac{\int_{\sigma} f_0(q) \exp \left[-\frac{1}{kT} \sum_{j,\alpha,\beta} \delta q_j \epsilon_{\alpha\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial q_j} \right)_{0,0} \right] d\sigma}{\int_{\sigma} f_0(q) d\sigma} \quad (36)$$

If the exponentials in equation (34) are expanded and only the first two terms in each expansion are retained,

$$\Gamma = \Gamma_u g(\epsilon) \frac{1 - \frac{1}{kT} \sum_{j,\alpha,\beta} \langle \delta q_j \rangle_{\sigma} \epsilon_{\alpha\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial q_j} \right)_{\ddagger,0}}{1 - \frac{1}{kT} \sum_{j,\alpha,\beta} \langle \delta q_j \rangle_{\sigma} \epsilon_{\alpha\beta} \left(\frac{\partial^2 \varphi}{\partial \epsilon_{\alpha\beta} \partial q_j} \right)_{0,0}} \quad (37)$$

However, in both the activated and normal states, the average displacement of an atom from its mean position is zero; that is,

$$\langle \delta q_j \rangle_{\sigma} = \langle \delta q_j \rangle_{\sigma=0}$$

and equation (37) reduces to

$$\Gamma = \Gamma_u g(\epsilon) \quad (38)$$

If the quadratic terms in the strain in equation (30) are neglected relative to the linear terms, substituting equation (30) into equation (34) gives

$$\Gamma_s = \Gamma_u \exp \left[-\sum_{\alpha\beta} \left(\frac{\partial \varphi}{\partial \epsilon_{\alpha\beta}} \right)_{\ddagger,0} \epsilon_{\alpha\beta} / kT \right] \quad (39)$$

Equation (39) shows that the jump frequency has a simple exponential dependence on the strains and that this dependence is controlled by the derivatives of the potential energy with respect to the strains evaluated at the saddle point of the activated state.

Equation (39) gives the general relation between the jump frequency and the strain that will be used in this report. If the strain matrix and the interatomic forces are known, the effect of the strain on the jump frequency can be computed.

To illustrate the application of equation (39), three special cases will be considered:

(1) Uniform compression or expansion in which

$$\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz} = \epsilon \quad (40)$$

(all other strains = 0)

(2) Simple shear in which

$$\epsilon_{xy} = \epsilon_{yx} = \epsilon_s \quad (41)$$

(all other strains = 0)

(3) Simple elastic tension or compression in the x -direction, in which

$$\left. \begin{aligned} \epsilon_{xx} &= \epsilon_L \\ \epsilon_{yy} &= \epsilon_{zz} = -\mu \epsilon_L \end{aligned} \right\} \quad (42)$$

where μ is Poisson's ratio.

For these three cases, equation (39) gives:
For uniform compression or expansion,

$$\Gamma_s = \Gamma_u \exp \left[-\frac{3\epsilon}{kT} \left(\frac{\partial \varphi}{\partial \epsilon} \right)_{\epsilon,0} \right] \quad (43)$$

For simple shear,

$$\Gamma_s = \Gamma_u \exp \left[-\frac{2\epsilon_s}{kT} \left(\frac{\partial \varphi}{\partial \epsilon_s} \right)_{\epsilon_s,0} \right] \quad (44)$$

For simple elastic tension or compression in the x -direction,

$$\Gamma_s = \Gamma_u \exp \left[-\frac{\epsilon_L}{kT} \left(\frac{\partial \varphi}{\partial \epsilon_L} \right)_{\epsilon_L,0} + \frac{2\mu\epsilon_L}{kT} \left(\frac{\partial \varphi}{\partial \epsilon_L} \right)_{\epsilon_L,0} \right] \quad (45)$$

Since strong repulsive forces come into play as the diffusing atom moves to the activated position, the derivatives in equation (39) and equations (43) to (45) are all negative. Thus, negative strains, corresponding to a compression of the lattice, decrease the jump frequency; and positive strains, corresponding to an expansion of the lattice, result in an increase in the jump frequency. This conclusion is in accord with what is expected on a simple physical basis.

The preceding equations are in agreement with the results of reference 9. On the basis of a simple model, which takes into account only nearest neighbor interaction, the effect of internal strains resulting from impurity atoms on the diffusion coefficient was computed (ref. 9), and it was found that the diffusion coefficient is an exponential function of the strain.

DEPENDENCE OF VACANCY CONCENTRATION ON STRAIN

It was pointed out in the section BASIC EQUATIONS OF DIFFUSION THEORY that the quantity n appearing in the generalized Fick's laws (eqs. (17) and (19)) has a different interpretation for different mechanisms of diffusion. For dilute interstitial diffusion, $n=1$ provided there are no sources of interstitials, and $\nabla n=0$ whether or not the system is strained. For diffusion by a vacancy mechanism, however, n is the atomic fraction of vacancies in the crystal given by

$$n = \frac{n_v}{N_T} \quad (46)$$

where

n_v vacancy concentration

N_T total number of lattice sites per cc

It is therefore necessary to investigate the variation of n_v with strain.

The concentration of vacancies in a crystal at equilibrium is given by

$$n_v = N_T \exp (-\Delta G_v/kT) \quad (47)$$

where

n_v vacancy concentration in the absence of strain

ΔG_v Gibb's free energy of formation of a vacancy

In a strained system, the free energy of formation of a vacancy may be different from that in an unstrained system, so that the vacancy concentration depends on the strain.

If the strains are constant in time, the vacancy concentration is also constant in time. However, during plastic deformation, vacancies are produced at a rate that depends on the strain rate (ref. 10). The general equation for the vacancy concentration is then

$$n_v^s = \bar{n}_x + N_T \exp (-\Delta G_v^s/kT) \quad (48)$$

where

\bar{n}_x excess average concentration of vacancies arising from the plastic strain

ΔG_v^s Gibb's free energy of formation of a vacancy in the strained system

The analysis in this section consists of two parts: (1) the effect of static strains on the free energy of vacancy formation, and (2) the effect of plastic flow on \bar{n}_x .

The Helmholtz free energy A of a perfect crystal is given by statistical mechanics as

$$\exp (-A/kT) = \int \dots \int \exp (-\psi_0/kT) \prod_{j=1}^{3N} dp_j dq_j \quad (49)$$

for a system of N particles, where ψ_0 is the energy of the system expressed as a function of the coordinates q_j and momenta p_j . For a crystal containing a single vacancy, the Helmholtz free energy is given by

$$\exp (-A_v/kT) = \int \dots \int \exp (-\psi_v/kT) \prod_{j=1}^{3N} dp_j dq_j \quad (50)$$

where ψ_0 and ψ_v are the energies of the system in the perfect and imperfect crystals, respectively.

Therefore, since $\Delta G = \Delta A + P\Delta V$, the Gibb's free energy of vacancy formation is given by

$$\exp(-\Delta G_v/kT) = \frac{\int \dots \int \exp(-\psi_i/dT) \prod_{j=1}^{3N} dp_j dq_j}{\int \dots \int \exp(-\psi_0/dT) \prod_{j=1}^{3N} dp_j dq_j} \exp(-P\Delta V_v/kT) \quad (51)$$

where

P = pressure

ΔV_v = volume change upon formation of a vacancy

If the phase integral is separated into configuration and momentum integrals, assuming the classical statistics of a crystal vibrating with normal mode frequencies, equation (51) becomes

$$\exp(-\Delta G_v/kT) = \frac{\int \exp(-\varphi_i/kT) dq \prod_j (v_0)_j}{\int \exp(-\varphi_0/kT) dq \prod_j (v_v)_j} \times \exp(-P\Delta V_v/kT) \quad (52)$$

where $(v_0)_j$ is the vibration frequency of the j^{th} vibrational mode in the perfect crystal, and $(v_v)_j$ is the frequency of the j^{th} vibrational mode in the crystal containing a vacancy. The integrals in equation (52) are for the entire configuration space.

In a strained crystal, the free energy of vacancy formation is given by an equation analogous to equation (52):

$$\exp(-\Delta G_v^s/kT) = \frac{\int \exp(-\varphi_i^s/kT) dq \prod_j (v_0^s)_j}{\int \exp(-\varphi_0^s/kT) dq \prod_j (v_v^s)_j} \times \exp(-P\Delta V_v^s/kT) \quad (53)$$

where the index s refers to the strained crystal.

An estimate of the effect of strain on the vibration frequencies can be made from Gruneisen's relation (ref. 11)

$$\frac{d \ln \nu}{d \ln V} = -\gamma \quad (54)$$

where

V = volume

γ = positive constant

Integrating equation (54) for each of the vibrational modes as the crystal goes from the unstrained to the strained state yields

$$\left. \begin{aligned} \frac{(v_0^s)_j}{(v_0)_j} &= \left(1 + \frac{\Delta V}{V}\right)^{-\gamma} \\ \frac{(v_v^s)_j}{(v_v)_j} &= \left(1 + \frac{\Delta V}{V}\right)^{-\gamma} \end{aligned} \right\} \quad (55)$$

It is evident that Gruneisen's relation leads to an equality of the products of frequency ratios in the strained and unstrained systems, so that combining equations (52) and (53) gives

$$\exp\left[-\frac{1}{kT}(\Delta G_v^s - \Delta G_v)\right] = \frac{\int \exp(-\varphi_i^s/kT) dq \int \exp(-\varphi_0/kT) dq}{\int \exp(-\varphi_0^s/kT) dq \int \exp(-\varphi_i/kT) dq} \times \exp[-(P\Delta V_v^s - P\Delta V_v)/kT] \quad (56)$$

The volume difference $(\Delta V_v^s - \Delta V_v)$ is given by

$$\begin{aligned} (\Delta V_v^s - \Delta V_v) &= (V_v^s - V_s) - (V_v - V) \\ &= (V_v^s - V_v) - (V_s - V) \end{aligned}$$

where

V = volume of perfect unstrained crystal

V_s = volume of perfect strained crystal

V_v = volume of unstrained crystal containing a vacancy

V_v^s = volume of strained crystal containing a vacancy

For small strains, the volume change resulting from the strain should be relatively insensitive to whether or not the crystal contains a vacancy. The volume differences $(V_v^s - V_v)$ and $(V_s - V)$ are therefore very nearly equal, and it is sufficiently accurate to take the difference $(\Delta V_v^s - \Delta V_v)$ equal to zero, so that the pressure-volume terms can be dropped from equation (56).

If the potential-energy functions φ_v^s and φ_0^s are now expanded in terms of the strains and the atomic displacements about the set of points corresponding to zero strains and mean atomic positions in the imperfect and perfect crystal, respectively, results analogous to equations (22) and (23) are obtained. Continuing the analysis leading to equation (39) shows that, to the first

order, the free energy of vacancy formation depends upon the derivatives of the potential energy with respect to the strains, evaluated at the points in configuration space corresponding to the atoms in their mean positions in the perfect and imperfect crystals. However, the states corresponding to the perfect and imperfect unstrained crystals when all the atoms are in their mean positions are both equilibrium states in which the systems are in potential wells with respect to both atomic coordinates and strains. Thus, the first derivatives are all zero and the free energy of formation of a vacancy is independent of the strains to a first-order approximation:

$$\Delta G_v^s \simeq \Delta G_v$$

The terms quadratic in the strains are, of course, not zero.

The analysis shows, therefore, that the jump frequency is more sensitive to strains than the energy of vacancy formation. In any diffusion process, the effect of strain is felt most strongly through the jump frequency, and for static strains this is usually the only factor that must be considered. Thus, to the first order in the strains, equation (48) may be written in the simple form

$$n_v^s = \bar{n}_v + N_T \exp(-\Delta G_v/kT)$$

The only problem remaining is to calculate the effect of plastic flow on \bar{n}_v .

Theory and experiment both indicate (refs. 2, 10, and 12) that, for simple types of deformation, the number of vacancies produced by plastic strain is proportional to the strain rate. In this report only simple plastic deformations that can be described by a single strain parameter are considered, including tension, compression, and shear. Accordingly, for the production rate of vacancies during plastic flow it is assumed that

$$\dot{n}_v = K_1 \dot{\epsilon} \quad (57)$$

where

$\dot{\epsilon}$ strain rate
 K_1 a constant

Since the vacancy concentration during plastic flow is greater than the thermodynamic equilibrium value, the excess vacancies will tend to precipitate out of the crystal matrix. It has been

shown that vacancy condensation is most probably a heterogeneous nucleation process (refs. 13 and 14) in which the vacancies precipitate at imperfections in the crystal such as grain boundaries, foreign inclusions, and voids. For such a mechanism it is reasonable to postulate that vacancies are removed from the lattice by a first-order process. That is, the rate of destruction is given by

$$\dot{n}_v = -K_2 \bar{n}_v \quad (58)$$

so that the differential equation governing the vacancy concentration is

$$\frac{d\bar{n}_v}{dt} = K_1 \dot{\epsilon} - K_2 \bar{n}_v \quad (59)$$

where

t time
 K_2 a constant

On a microscopic scale, it is obvious that the excess concentration of vacancies may vary considerably from one point in the crystal to another, depending upon the distribution of the imperfections in the lattice, which act as vacancy sources and sinks. However, in macroscopic diffusion experiments, interest lies in the overall average vacancy concentration. Accordingly, a bar is placed over n_v to indicate the space average of the vacancy concentration.

Integration of equation (59) gives

$$\bar{n}_v = \frac{K_1 \dot{\epsilon}}{K_2} [1 - \exp(-K_2 t)] \quad (60)$$

and equation (48) becomes

$$n_v^s = \frac{K_1 \dot{\epsilon}}{K_2} [1 - \exp(-K_2 t)] + N_T \exp(-\Delta G_v/kT) \quad (61)$$

The mode of production of vacancies by moving dislocations is discussed in some detail in references 10 and 12. As pointed out in these references, a number of possible mechanisms exist by which moving dislocations can generate vacancies. At present it does not seem possible to perform an accurate calculation of the rate of production of vacancies, and therefore K_1 must be treated as an empirical parameter to be determined by experiment. However, it can be noted that, if the generation mechanism involves dislocation climb, K_1 will be proportional to the coefficient

of self-diffusion as well as to the dislocation density. If a purely geometric mechanism is involved, K_1 will depend only upon the dislocation density. Thus, for production by a geometric mechanism,

$$K_1 = c_1$$

and for production by a thermally activated mechanism,

$$K_1 = c_2 \exp(-E/kT)$$

where

c_1, c_2 temperature-independent constants
 E energy of activation for self-diffusion

The rate of destruction of vacancies is determined by K_2 . References 13, 15, and 16 are concerned with calculating the rate of absorption of vacancies by various types of vacancy sinks, and the remaining discussion of this section is largely an extension and development of this work.

The constant K_2 depends on the nature of the vacancy sinks in the material. Obviously, different kinds of vacancy sinks are possible. Thus, a foreign inclusion may collect vacancies and give rise to a void that acts as a spherical or ellipsoidal sink, and large grain boundaries may act as two-dimensional sinks. Dislocations may act as sinks for vacancies in two ways: If the energy of interaction between a vacancy and a dislocation line is great enough, a vacancy becomes immobile and is essentially removed from the diffusion region when it gets closer to the dislocation line than some specified distance R_o . The dislocation line then gives a rise to a cylindrical sink of radius R_o . This type of sink is proposed in reference 16. If the energy of interaction between a dislocation and a vacancy is large only at certain discrete points along the dislocation line, such as dislocation jogs, then K_2 depends on the frequency of collision between a vacancy and a jog. This type of sink is postulated in reference 13 in studies of precipitation of vacancies during diffusion. Thus, four types of idealized vacancy sinks are considered: spherical, platelike, cylindrical, and discrete-point sinks.

SPHERICAL VACANCY SINKS

It is assumed that a spherical sink of radius R_o is located at the center of a spherical region of radius R . During plastic flow, the production

rate of vacancies is $K_1\dot{\epsilon}$, so that the spherically symmetric steady-state diffusion equation is

$$\frac{D_v}{r^2} \frac{d}{dr} \left(r^2 \frac{dn_v^o}{dr} \right) + K_1 \dot{\epsilon} = 0 \quad (62)$$

where

D_v diffusion coefficient for vacancies
 r radial distance from the center
 o steady-state conditions

For the purpose of this calculation, the effect of the deformation on the coordinates in equation (62) is neglected, and it is also assumed that D_v is independent of position.

The boundary conditions chosen for the solution of equation (62) are

$$\left. \begin{aligned} n_v^o(R_o, t) &= 0 \\ \left(\frac{dn_v^o}{dr} \right)_{r=R} &= 0 \end{aligned} \right\} \quad (63)$$

Equations (63) imply that the sink is a perfect absorber of excess vacancies and that the sinks are uniformly distributed through the crystal in such a way that the distance between them is $2R$.

The solution of equation (62) with the boundary conditions given by equations (63) is

$$n_v^o = \frac{K_1 \dot{\epsilon}}{3D_v} \left(\frac{R^3}{R_o} - \frac{R^3}{r} + \frac{R_o^2}{2} - \frac{r^2}{2} \right) \quad (64)$$

The average concentration \bar{n}_v^o throughout the spherical volume of radius R is given by

$$\bar{n}_v^o = \frac{3 \int_{R_o}^R n_v^o r^2 dr}{(R^3 - R_o^3)} \quad (65)$$

Performing the integration in equation (65) gives

$$\bar{n}_v^o = \frac{K_1 \dot{\epsilon}}{D_v} \left[\frac{R^3}{3R_o} - \frac{R^3(R^2 - R_o^2)}{2(R^3 - R_o^3)} + \frac{R_o^2}{6} - \frac{1}{10} \frac{(R^5 - R_o^5)}{(R^3 - R_o^3)} \right] \quad (66)$$

If $R_o \ll R$, so that the distance between sinks is much larger than their radius, then, at steady state,

$$\bar{n}_v^o = \frac{K_1 \dot{\epsilon}}{3D_v} \frac{R^3}{R_o} \quad (67)$$

But from equation (59), the steady-state condition gives

$$K_1 \dot{\epsilon} = K_2 \bar{n}_v^o \quad (68)$$

which, combined with equation (67), gives

$$K_2 = \frac{3R_o D_v}{R^3} \quad (69)$$

or, if there are f sinks per unit volume,

$$K_2 = 4\pi R_o f D_v \quad (70)$$

PLATELIKE SINKS

For platelike sinks of thickness L_o and a distance $2L$ apart, the boundary-value problem analogous to equations (62) and (63) is

$$\left. \begin{aligned} D_v \frac{d^2 n_x^o}{dx^2} + K_1 \dot{\epsilon} &= 0 \\ n_x^o(L_o) &= 0 \\ \left(\frac{dn_x^o}{dx} \right)_{x=L} &= 0 \end{aligned} \right\} \quad (71)$$

where x is the perpendicular distance from the plate. The solution of equation (71) is

$$n_x^o = \frac{K_1 \dot{\epsilon}}{D_v} \left[(Lx - LL_o) - \frac{1}{2}(x^2 - L_o^2) \right] \quad (72)$$

and if $L_o \ll L$, the average concentration is

$$\bar{n}_x^o = \frac{K_1 \dot{\epsilon} L^2}{3D_v} \quad (73)$$

$$K_2 = \frac{2D_v}{L^2} \quad (74)$$

or, if the area of the platelike sinks is approximately L^2 (as would be the case in a material of uniform grain size), then,

$$K_2 \simeq 2D_v f L \quad (75)$$

CYLINDRICAL SINKS

For cylindrical sinks, the boundary-value problem becomes

$$\left. \begin{aligned} \frac{1}{r} \frac{d}{dr} \left(r D_v \frac{dn_x^o}{dr} \right) + K_1 \dot{\epsilon} &= 0 \\ n_x^o(r_o) &= 0 \\ \left(\frac{dn_x^o}{dr} \right)_{r=r} &= 0 \end{aligned} \right\} \quad (76)$$

where

r_o radius of cylindrical sink
 $2r_1$ distance between sinks

The solution of equation (76) is

$$n_x^o = \frac{K_1 \dot{\epsilon}}{D_v} \left[\frac{r_1^2}{2} \ln \frac{r}{r_o} - \left(\frac{r^2}{4} - \frac{r_o^2}{4} \right) \right] \quad (77)$$

and for $r_o \ll r_1$,

$$\bar{n}_x^o = \frac{K_1 \dot{\epsilon}}{2D_v} r_1^2 \ln \frac{r_1}{r_o} \quad (78)$$

and

$$K_2 = \frac{2D_v}{r_1^2 \ln \frac{r_1}{r_o}} \quad (79)$$

If the sinks are dislocations of length l , the volume per sink is $\pi r_1^2 l$ and equation (79) can be expressed as

$$K_2 = \frac{2\pi D_v f l}{\ln \frac{r_1}{r_o}} \quad (80)$$

But, fl is the number of dislocation lines per square centimeter, that is, the dislocation density N_D , so that

$$K_2 = \frac{2\pi D_v N_D}{\ln \frac{r_1}{r_o}} \quad (81)$$

DISCRETE-POINT SINKS

If the vacancies are destroyed by an atomic collision process, as would be the case if only certain points, such as dislocation jogs, are effective in trapping vacancies, the rate of vacancy destruction is proportional to the collision frequency between vacancies and jogs.

The jump frequency of a vacancy is roughly D_v/λ^2 ; and, if C_j is the dislocation jog concentration, the collision rate between excess vacancies and jogs is

$$\frac{D_v}{\lambda^2} n_x \frac{C_j}{N_T} \quad (82)$$

where C_j/N_T is the probability that, when a vacancy jumps, it runs into a jog. If it is assumed that all collisions result in a destruction of the excess vacancy,

$$K_2 = \frac{D_v C_j}{\lambda^2 N_T} \quad (83a)$$

Inspection of the various expressions for K_2 shows that K_2 is proportional to the diffusion coefficient for vacancies and to the concentration of vacancy sinks, and depends on the geometric character of the sink.

In addition to the mechanisms involving migration to sinks, vacancies may disappear by combining with interstitials. Since interstitials are much more mobile than vacancies (ref. 16, ch. 5), only the diffusion rate of the interstitials must be considered in the recombination process. The jump frequency of an interstitial is D_i/λ^2 , where D_i is the diffusion coefficient for the motion of interstitial atoms. If the concentration of interstitials is n_i , K_2 is given by

$$K_2 = \frac{D_i n_i}{\lambda^2 N_T} \quad (83b)$$

Thus, if the vacancies are destroyed by recombination with interstitials, K_2 is proportional to the diffusion coefficient for interstitials rather than to the diffusion coefficient for vacancies.

In an actual crystal, several of the production and annealing mechanisms may be operating simultaneously, in which case the constants K_1 and K_2 are given by sums of the special cases described previously.

DIFFUSION COEFFICIENT AS FUNCTION OF STATIC AND DYNAMIC STRAINS

In the previous sections, the theoretical framework for an analysis of the effect of strain on diffusion has been developed. In this section, the previous results are combined to give the final functional dependence of the diffusion coefficient on the strains.

From equation (19) it is evident that for an isotropic solid under homogeneous strain the diffusion coefficient for the flow of species N is given by

$$D_s = \alpha \lambda_s^2 n_s \Gamma_s \quad (84)$$

where

λ_s lattice parameter

α constant that is determined by the crystal structure

The subscript s refers to the strained crystal.

Four special cases of the general equation (84) are considered:

- (1) Diffusion by an interstitial mechanism in the presence of static strain (strain rate, zero)

- (2) Diffusion by a vacancy mechanism in the presence of static strains
- (3) Diffusion by an interstitial mechanism during plastic deformation (strain rate not zero)
- (4) Diffusion by a vacancy mechanism during plastic deformation.

The four diffusion coefficients corresponding to these four cases will be labeled $D_i^{(1)}$, $D_v^{(2)}$, $D_i^{(3)}$, and $D_v^{(4)}$, respectively.

For case (1), $n_s=1$ as discussed in the section DEPENDENCE OF VACANCY CONCENTRATION ON STRAIN, and Γ_s is given by one of the equations (39) or (43) to (45). For the purposes of this discussion it is assumed that the deformation is a uniform lattice contraction, so that equation (43) gives the dependence of the jump frequency on strain. The extension to other types of strain is obvious. Using equation (43) and the fact that the strained lattice parameter is related to the unstrained lattice parameter by the factor $(1+\epsilon)$ for case (1) yields

$$D_i^{(1)} = \alpha \lambda^2 (1+\epsilon)^2 \Gamma_u \exp \left[-\frac{3\epsilon}{kT} \left(\frac{\partial \varphi}{\partial \epsilon} \right)_{\epsilon=0} \right] \quad (85)$$

For case (2), the vacancy concentration is governed by equation (47), and to a first-order approximation is unaffected by strain. Since $n_s = n_v/N_T$, and for the homogeneous deformation case being considered Γ_s is given by equation (43), the diffusion coefficient for case (2) is given by

$$D_v^{(2)} = \alpha \lambda^2 \frac{n_v}{N_T} \Gamma_u (1+\epsilon)^2 \exp \left[-\frac{3\epsilon}{kT} \left(\frac{\partial \varphi}{\partial \epsilon} \right)_{\epsilon=0} \right] \quad (86)$$

Since plastic flow does not affect the number of interstitial sites, $n_s=1$ even in case (3), and a result identical to that of equation (85) is obtained:

$$D_i^{(3)} = \alpha \lambda^2 \Gamma_u [1+\epsilon(t)]^2 \exp \left[-\frac{3\epsilon(t)}{kT} \left(\frac{\partial \varphi}{\partial \epsilon} \right)_{\epsilon=0} \right] \quad (87)$$

A significant difference between equations (87) and (85) is that in equation (87) the strain, and therefore the diffusion coefficient, is a function of time. Also, in equation (85), the strain that must be considered is the actual lattice strain and not the observed macroscopic strain. For plastic deformations, these two strains are not, in general, equal.

For case (4), the vacancy concentration is given by equation (61). Thus, again using equation (43) and the fact that $n_s = n_v/N_T$ for case (4) gives

$$D_i^{(v)} = \alpha \lambda^2 \Gamma_u [1 + \epsilon(t)]^2 \exp \left[-\frac{3\epsilon(t)}{kT} \left(\frac{\partial \phi}{\partial \epsilon} \right)_{t,0} \right] \times \left\{ \frac{n_r}{N_T} \frac{K_1 \dot{\epsilon}}{K_2 N_T} [1 - \exp(-K_2 t)] \right\} \quad (88)$$

For interstitial diffusion, the diffusion coefficient in the unstrained case is

$$D^{(i)} = \alpha \lambda^2 \Gamma_u \quad (89)$$

and, for diffusion by a vacancy mechanism in the unstrained case,

$$D^{(v)} = \alpha \lambda^2 \Gamma_u \frac{n_r}{N_T}$$

Therefore, equations (85) to (88) may be written as

$$D_i^{(i)} = D^{(i)} [1 + \epsilon]^2 \exp \left[-\frac{3\epsilon}{kT} \left(\frac{\partial \phi}{\partial \epsilon} \right)_{t,0} \right] \quad (90)$$

$$D_i^{(v)} = D^{(v)} [1 + \epsilon]^2 \exp \left[-\frac{3\epsilon}{kT} \left(\frac{\partial \phi}{\partial \epsilon} \right)_{t,0} \right] \quad (91)$$

$$D_i^{(i)} = D^{(i)} [1 + \epsilon(t)]^2 \exp \left[-\frac{3\epsilon(t)}{kT} \left(\frac{\partial \phi}{\partial \epsilon} \right)_{t,0} \right] \quad (92)$$

$$D_i^{(v)} = D^{(v)} [1 + \epsilon(t)]^2 \exp \left[-\frac{3\epsilon(t)}{kT} \left(\frac{\partial \phi}{\partial \epsilon} \right)_{t,0} \right] \left\{ 1 + \frac{K_1 \dot{\epsilon}}{K_2 n_r} [1 - \exp(-K_2 t)] \right\} \quad (93)$$

These equations show how the effects of various types of strains on the diffusion coefficient can be taken into account for different diffusion mechanisms. The extension of this analysis to other diffusion mechanisms is completely analogous to the present development and will not be given here.

It should be noted that, in the expression for $D_i^{(v)}$, the strain rate in equation (93) is the macroscopic strain rate, although the strain $\epsilon(t)$ is the microscopic lattice strain.

COMPARISON OF THEORY WITH EMPIRICAL DATA

The theory presented in this report makes a number of predictions that can be checked by existing experimental data. In this section, an analysis of the validity of the theory is made by

comparing the theoretical results with diffusion data. The equations developed thus far are not always in the form most suitable for comparison with experiment. Whenever necessary, therefore, the equations will be transformed into a convenient form.

The only literature data available for testing equation (91) are concerned with the effect of hydrostatic pressure on the diffusion coefficient.

The experimental data usually give the diffusion coefficient as a function of pressure, so that, from the pressure-volume relation of the material, the data can be obtained as a function of strain. Since pressure-volume data are generally given in terms of $\Delta V/V_o$, it is convenient to express ϵ as a volume strain (V_o is the volume of zero pressure). The strain ϵ is

$$\epsilon = \frac{\lambda_s - \lambda}{\lambda} = \frac{\Delta \lambda}{\lambda} \quad (94)$$

so that, in terms of volume strain,

$$\epsilon = \frac{1}{3} \frac{\Delta V}{V_o} \quad (95)$$

for small strains. Therefore, using equations (94) and (95) and also the fact that

$$\lambda_s^2 = \lambda^2 \left(1 + \frac{\Delta V}{V_o} \right)^{2/3} \quad (96)$$

changes equation (91) to

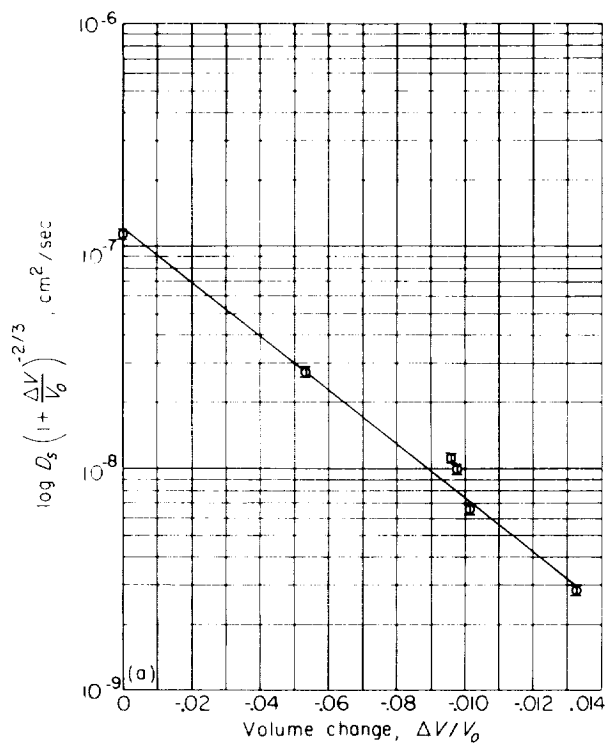
$$D_i^{(v)} \left(1 + \frac{\Delta V}{V_o} \right)^{-2/3} = D^{(v)} \exp \left[-\frac{\Delta V}{V_o kT} \left(\frac{\partial \phi}{\partial \epsilon} \right)_{t,0} \right] \quad (97)$$

Therefore, it is evident that a plot of $\ln D_i^{(v)} (1 + \Delta V/V_o)^{-2/3}$ against $\Delta V/V_o$ should be linear with a slope m given by

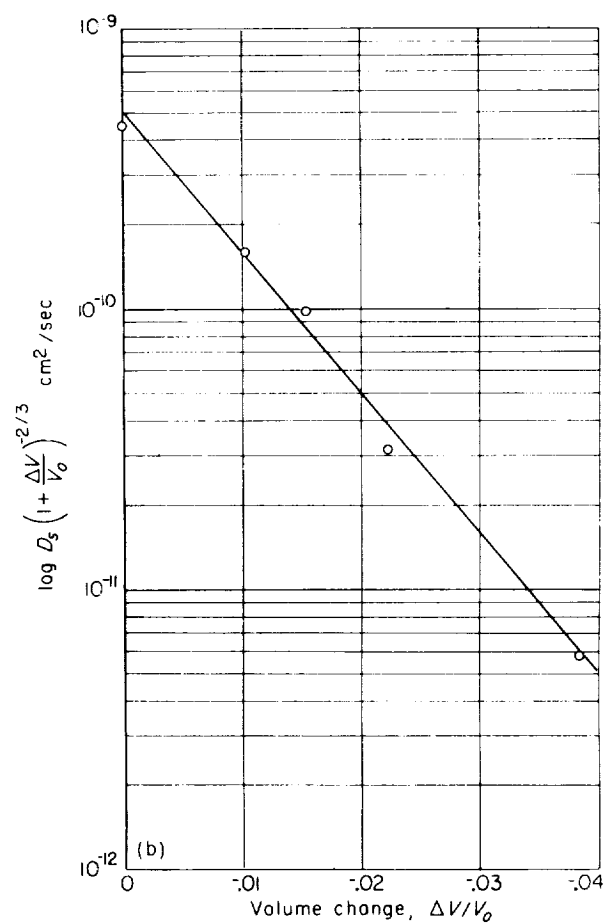
$$m = - \left(\frac{\partial \phi}{\partial \epsilon} \right)_{t,0} \frac{1}{kT} \quad (98)$$

and an intercept given by $\ln D^{(v)}$.

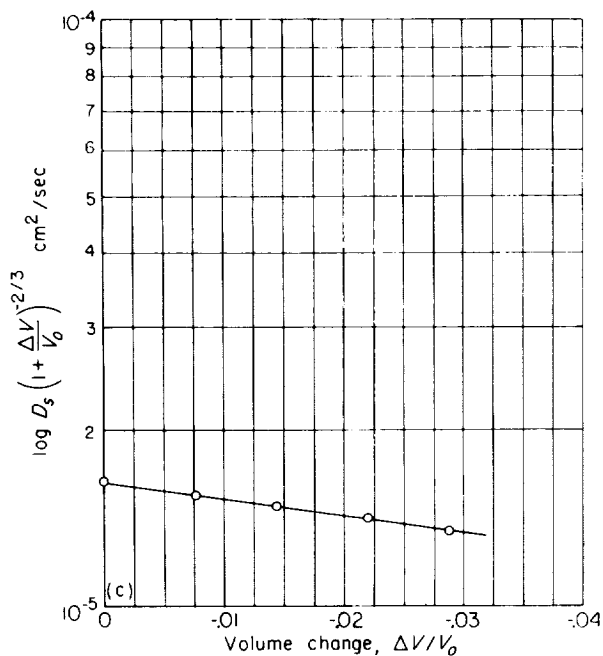
Several investigators have obtained data on the variation of the diffusion coefficient with pressure that are suitable for testing equation (97). Reference 4 presents data for the self-diffusion coefficient as a function of pressure for sodium, phosphorus, and mercury up to pressures of 12,000, 4000, and 8000 atmospheres, respectively. The self-diffusion coefficient of liquid gallium up



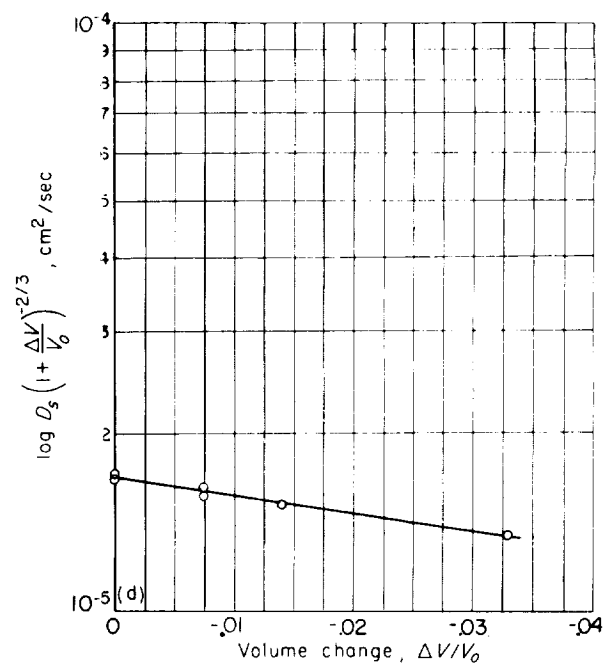
(a) Sodium at 363° K.



(b) White phosphorus at 314° K.



(c) Liquid mercury at 303° K.



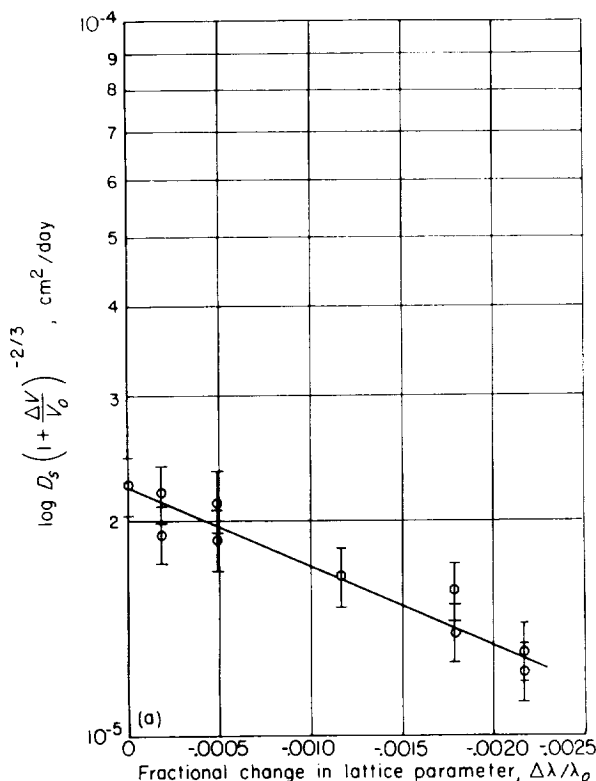
(d) Liquid gallium at 303° K.

FIGURE 1. Variation of $\log D_s \left(1 + \frac{\Delta V}{V_0}\right)^{-2/3}$ plotted against volume change, $\Delta V/V_0$, for self-diffusion of various elements.

to pressures of 10,000 atmospheres is given in reference 17. The self-diffusion coefficient for single crystal zinc up to pressures of 10,000 atmospheres for diffusion in the directions parallel to and perpendicular to the c -axis is determined in reference 1.

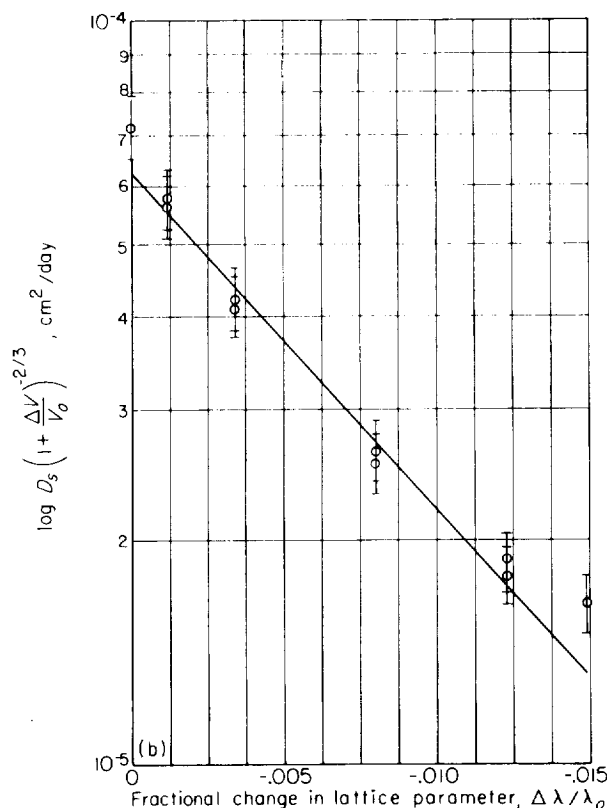
The electric conductivities of silver chloride and silver bromide have been measured as a function of pressure up to 300 atmospheres (ref. 18). Since the conductivity is proportional to the diffusion coefficient of the silver ion by the Nernst-Einstein relation, the data of reference 18 are suitable for testing equation (97).

Plots of the variation of the quantity $\log D_s^{(p)}(1 + \Delta V/V_0)^{-2/3}$ against $\Delta V/V_0$ for the self-diffusion of sodium, phosphorus, mercury, and gallium are shown in figure 1. The quantities $\log D_s^{(p)}(1 + \Delta V/V_0)^{-2/3}$ for single crystal zinc were plotted against the fractional change in lattice parameter $\Delta\lambda/\lambda_0$, since this is a more natural



(a) Zinc at 580° K, perpendicular to c -axis.

FIGURE 2. Variation of $\log D_s (1 + \Delta V/V_0)^{-2/3}$ plotted against fractional change in lattice parameter $\Delta\lambda/\lambda_0$ for self-diffusion in zinc.



(b) Zinc at 580° K, parallel to c -axis.

FIGURE 2. Concluded. Variation of $\log D_s (1 + \Delta V/V_0)^{-2/3}$ plotted against fractional change in lattice parameter $\Delta\lambda/\lambda_0$ for self-diffusion in zinc.

unit for discussing diffusion in anisotropic crystals, and the linear compressions perpendicular and parallel to the c -axis are available. The zinc data are plotted in figure 2.

Figure 3 gives $\log 1/R$ plotted against $\Delta V/V_0$ for silver chloride and silver bromide, where R is the resistivity. The volume change $\Delta V/V_0$ is small enough for the pressure range considered so that $(1 + \Delta V/V_0)^{-2/3}$ does not appreciably affect the results and can be ignored.

Compressibility data (refs. 19 to 23) were used to obtain the appropriate value of $\Delta V/V_0$ for zinc, sodium, mercury, silver chloride, and silver bromide. For gallium, $\Delta V/V_0$ was computed from the data of reference 22 assuming that the form of $\Delta V/V_0$ as a function of pressure is the same as that for mercury. The values of $\Delta V/V_0$ for white phosphorus were computed from data from reference 24 assuming that the variation of

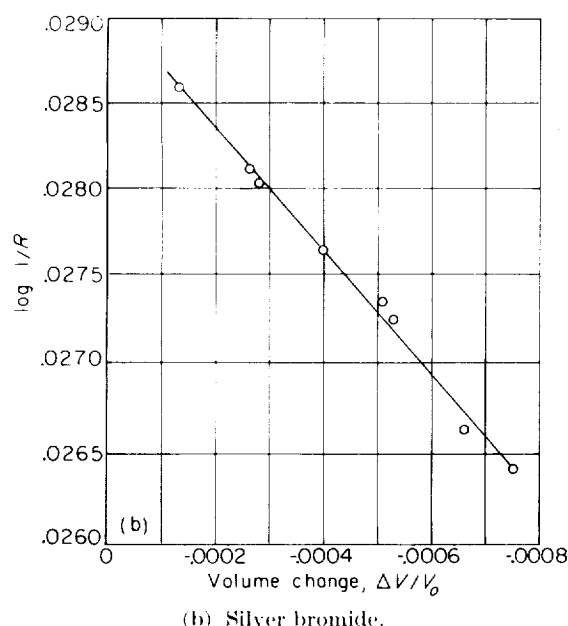
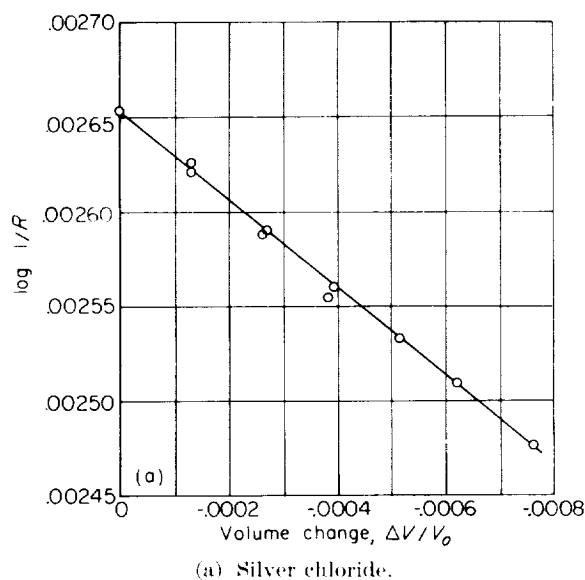


FIGURE 3. Variation of $\log 1/R$ plotted against volume change $\Delta V/V_0$ for mobility of silver at 573°K .

the fractional volume change with pressure has the same form as that observed in reference 25 for black and red phosphorus.

In all cases, the available compressibility data were extrapolated to the diffusion temperature.

The linearity of the plots presented in figures 1 to 3 shows that the form of equation (97) is valid for those systems investigated within the probable

inaccuracies of the experiments and the calculations.

The slopes of the plots given in figures 1 to 3 are related to the interatomic forces through equation (97). If the repulsive potential is steep for a certain metal, that is, the atoms are "hard," then for a given atom displacement arising from a lattice strain, the rate of change of the potential energy with strain is much greater than for a similarly strained crystal containing "soft" atoms. Thus, $(\partial\phi/\partial\epsilon)_{\epsilon,0}$ should be large for hard atoms and small for atoms having slowly varying potential functions. The quantity $-1/k (\partial\phi/\partial\epsilon)_{\epsilon,0} = mT$ has been calculated from the slopes of the plots of $D^{(r)}(1+\Delta V/V_0)^{-2/3}$ plotted against $\Delta V/V_0$ and the absolute temperatures of the available diffusion experiments. Table I summarizes these values of m and nT .

TABLE I. COMPARISON OF VALUES OF mT FOR VARIOUS METALS

Metal	Temperature, T , $^\circ \text{K}$	m	mT
Sodium	363	27.9	10,120
Zinc (\perp)	580	86.6	50,200
Zinc (\parallel)	580	34.7	20,100
Mercury (liquid)	303	6.5	1,970
Gallium (liquid)	303	6.5	1,970
Silver in silver chloride	573	91.9	52,600
Silver in silver bromide	573	128.0	73,000

The lowest values of mT are those for mercury and gallium. This is to be expected, since they have relatively "soft" potential functions, and being in the liquid state, their atoms are highly mobile so that they can adjust to the motion of the diffusing atom to give the lowest possible values to the interatomic forces. The values of mT for the silver halides are among the highest, and this is entirely reasonable in view of the steeply rising repulsive potential a silver ion meets as it migrates from one stable position to the next. In zinc, mT is much larger for diffusion perpendicular to the c -axis than for diffusion parallel to the c -axis. This is in accord with the fact that the nearest neighbor distances are closer in the perpendicular position, so that when an atom migrates

to the activated position, the change in the interatomic forces is greater for a corresponding process in a direction parallel to the c -axis. Of all the solids listed, sodium has the lowest value of mT . The interatomic potential varies relatively slowly for sodium; in fact, recent calculations (unpublished NASA data) show that the potential well is so broad that the pairwise potential is repulsive to distances as far out as 1.4 times the nearest neighbor distance in solid sodium. Thus the low value of mT for sodium is in agreement with its interpretation in terms of the interatomic forces.

The fact that mT is so much smaller for the liquid metals than for any of the solids including sodium is indicative of the difference in the mechanism of diffusion in liquids and solids. In a liquid, the atoms are not constrained to remain at lattice positions, so that diffusion occurs by a cooperative process involving the migrating atom and its nearest neighbors. Thus, the change in the interatomic forces can be kept to a minimum throughout the diffusion process, and consequently mT would be very low.

DEPENDENCE OF DIFFUSION COEFFICIENT ON STRAIN RATE

In the absence of strain, the diffusion coefficient D is given by the usual expression

$$D = \alpha \lambda^2 \nu n \exp(-\Delta G/kT) \quad (99)$$

For diffusion by a vacancy mechanism, n is the atomic fraction of vacancies in the crystal at equilibrium. In a crystal undergoing plastic deformation, the diffusion coefficient is

$$D_s^{(e)} = \alpha \lambda_s^2 n_s \nu_s \exp(-\Delta G_s/kT) \quad (100)$$

As usual, the subscript s refers to the strained system.

If it could be postulated that, at the stress levels at which plastic flow occurs at diffusion temperatures, the effects of the strain on the quantities λ , ν , and ΔG are negligible compared with the effect of the strain rate on the vacancy concentration, then to a good approximation the ratio $D_s^{(e)}/D^{(e)}$ would be given by

$$\frac{D_s^{(e)}}{D^{(e)}} = \frac{n_s}{n} \quad (101)$$

This postulate is a reasonable one, since it is well known that moving dislocations produce large numbers of vacancies. Also, plastic flow occurs

by the displacement of large blocks of material as a result of dislocation motion, so that the microscopic strains defining the relative atomic positions are much smaller than the macroscopic strains. In fact, it is highly probable that the microscopic strains are always below the elastic limit of the material.

Recent measurements (unpublished NASA data) of the effect of dynamic plastic flow on the rate of diffusion of hydrogen through nickel substantiate this hypothesis. The diffusion coefficient has been found to be independent of the state of plastic strain for tensile strain rates of 0.02 to 0.4 hour⁻¹. Since hydrogen diffuses through nickel by an interstitial mechanism, any effect of strain on the diffusion coefficient must manifest itself through the quantities λ , ν , and ΔG . The hydrogen diffusion experiments can therefore be interpreted as indicating that the effect of plastic deformation on quantities other than the vacancy concentration is negligible.

For the simple types of dynamic strains discussed in the section DEPENDENCE OF VACANCY CONCENTRATION ON STRAIN, n_s/n is obtained by dividing equation (61) by equation (47), so that

$$\frac{D_s^{(e)}}{D^{(e)}} = 1 + \frac{K_1 \dot{\epsilon}}{K_2 n_s} [1 - \exp(-K_2 t)] \quad (102)$$

Equation (102) shows that D_s increases with time up to an asymptotic steady state at which

$$\frac{D_s^{(e)}}{D^{(e)}} = 1 + \frac{K_1 \dot{\epsilon}}{K_2 n_s} \quad (103)$$

The time required to reach the steady state depends upon the value of K_2 . In order to obtain an estimate of K_2 , it will be assumed that the predominant type of vacancy sink is a cylinder around a dislocation line, so that equation (81) is valid:

$$K_2 = \frac{2\pi D_s N_D}{\ln \frac{r_1}{r_o}} \quad (104)$$

Typical values of D_s at approximately 1000° C are in the range of 10⁻⁷ to 10⁻⁹ centimeter squared per second, and a value of about 10⁷ for $2\pi N_D / \ln (r_1/r_o)$ has been given in reference 26, so that K_2 is in the range of 1 to 10⁻². Consequently, the factor $[1 - \exp(-K_2 t)]$ reaches a value of 0.9 in a time somewhere between 0.04 and 4 minutes.

For the example stated, a diffusion experiment should last at least several hours if $D_e = 10^{-9}$, and at least several minutes if D_e is as high as 10^{-7} .

The only data available in the literature on the effect of plastic deformation on diffusion are for the case of iron over a restricted range of strain rates (refs. 2 and 3). Although the data are not extensive, and some doubt exists concerning the absolute magnitude of the effect (ref. 3), a linear relation between the diffusion coefficient and the strain rate seems to be valid. This is in agreement with the steady-state equation (103). In view of the scarcity of the data in this field, not much more can be said concerning the agreement of the theory with experiment. Additional experimental work in this area is highly desirable.

VOLUME OF ACTIVATION

From a comparison of equations (97), (98), and (100), the free energy of activation for diffusion in a system subjected to hydrostatic pressure varies with the volume strain according to

$$\Delta G_s = \Delta G - m \frac{\Delta V}{V_o} kT \quad (105)$$

since $v_s \approx v$ for small lattice strains. Applying the definition of the activation volume for small lattice strains gives

$$\Delta V_s = -mkT \left[\frac{\partial(\Delta V/V_o)}{\partial P} \right]_T \quad (106)$$

But,

$$\left(\frac{\partial \Delta V}{\partial P} \right)_T = -\beta \quad (107)$$

where β is the compressibility, so that the activation volume is given by

$$\Delta V_s = m\beta kT \quad (108)$$

Table II presents values of the activation volume calculated from equation (108) at atmospheric pressure for those systems for which data are available. Figure 4 is a comparison of the activation volume of self-diffusion in sodium calculated from equation (108) with the activation volume calculated in reference 4 from experimental data. The agreement is seen to be good.

TABLE II.—ACTIVATION VOLUMES FOR SELF-DIFFUSION OF VARIOUS METALS AT 1 ATMOSPHERE CALCULATED FROM EQUATION (108)

Metal	Temperature, T , ° K	Activation volume, ΔV_s , cc/g-atm	
		Calculated	Experimental
Sodium	363	12.3	12.3 (ref. 4)
Phosphorus (white)	314	71.7	30.0 (ref. 4)
Zinc (⊥)	580	3.0	4.9 (ref. 1)
Zinc ()	580	8.3	16.9 (ref. 1)
Mercury (liquid)	303	.62	.57 (ref. 4)
Gallium (liquid)	303	.62	.55 (ref. 16)
Silver in silver chloride	573	10.3	
Silver in silver bromide	573	13.7	

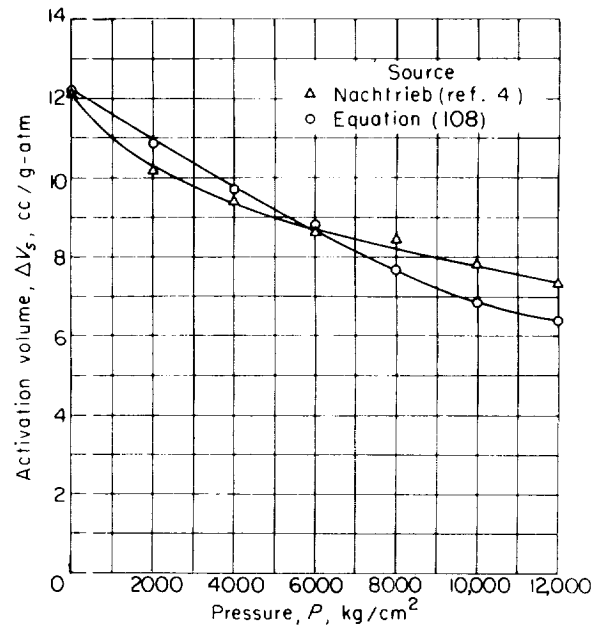


FIGURE 4. Activation volume plotted against pressure for self-diffusion of sodium at 362° K.

CONCLUSIONS

A theory was developed that relates diffusion rates to the state of strain of the material. Fick's laws of diffusion were generalized to include the

strain. The generalized equations differ from the ordinary diffusion equations in that the flux of diffusing material is proportional to terms containing the strain gradient as well as to terms containing the concentration gradient. In addition, a molecular-kinetic theory was developed that relates the diffusion coefficient to strain in terms of the atomic properties of the system.

The effect of dynamic plastic deformation on the diffusion coefficient was investigated by considering the rate of production of vacancies by moving dislocations and the rate of precipitations of vacancies at vacancy sinks. The resulting equation states that the diffusion coefficient is a linear function of the strain rate.

Several predictions that can be checked by existing experimental data may be made from the theory:

1. For diffusion as a function of hydrostatic pressure, the diffusion coefficient is an exponential function of the volume strain.

2. The rate of change of the diffusion coefficient with strain is related to the interatomic forces. The relation is explicit enough that the variation of the diffusion coefficient with pressure can be interpreted in terms of the interatomic potential-energy functions of the material.

3. For diffusion under hydrostatic pressure, the activation volume can be calculated from the compressibility and the rate of change of the diffusion coefficient with volume strain.

4. Dynamic plastic deformation increases the diffusion rate, the diffusion coefficient being linearly related to the strain rate at steady state.

In every case for which data are available, these conclusions are in agreement with experiment.

The general framework of the theory provides a basis for understanding the effect of strain on diffusion in terms of the molecular-kinetic properties of the system and should provide a valuable tool for comparing diffusion rates for different states of strain, as well as for investigating the mechanism of diffusion.

LEWIS RESEARCH CENTER

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
CLEVELAND, OHIO, September 2, 1958

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